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13. ABSTRACT (Maximum 200 Words) The electroluminescence of a number of conjugated macromolecules has been studied with particular reference to finding systems with high quantum yields. Various strategies have been investigated to optimize the light output from devices incorporating these polymers. The program included complementary studies of relevant optical and other physical properties of these materials.				
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ELECTRO-OPTICAL PROPERTIES OF POLYMER BLENDS: LASING,
ELECTROLUMINESCENCE AND PHOTOPHYSICS

GRANT AFOSR FA9550-06-1-0040

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TECHNICAL SUMMARY

Investigations concerning the synthesis, characterization and properties of electro-optical macromolecules have been completed. A wide range of structures based on conjugated main chains and focusing on providing high photo-luminescent and electroluminescent quantum yields were produced, and fabricated into opto-electronic devices. Relevant physical characterization of the polymers in terms of spectroscopic properties has been carried out.

PUBLICATIONS

A fraction of the investigations referred to have already been published. These include:

1. Chem.Phys.Chem., 6, 267-276 (2005) (V. Strehmel, A.M. Sarker, P.M. Lahti, M. Heydenreich, H. Wetzel, S. Haebel, B. Strehmel and F.E. Karasz) "One-and Two-Photon Photochemistry and Photophysics of Poly(arylene)s Containing a Biphenyl Moiety".
2. Thin Solid Films, 479, 249-253 (2005) (L. Liao, Y. Pang, L. Ding and F.E. Karasz) "Optical Properties of Poly[(1,4-phenylenevinylene)-alt-(1,3-phenylenevinylene)]s with cis-vinylene Structure and Short Side Chain".
3. J. Appl. Polym. Sci., 99, 3125-3129 (2006) (A. Cirpan and F.E. Karasz) "Indium Tin Oxide Nanoparticles as Anode for Light-Emitting Diodes".

4. Chem. Mater., 18, 560-566 (2006) (H.P. Rathnayake, A. Cirpan, P.M. Lahti and F.E. Karasz) "Optimizing LED Properties of 2, 7-Bis(phenylethenyl)fluorenes".
5. J. Polym. Sci., 44, 2307-2315 (2006) (L. Liao, A. Cirpan, L. Ding, Y. Pang and F.E. Karasz) "Efficient Blue-Green-Emitting Poly[(5-diphenylamino-1,3-phenylenevinylene)-*alt*-(2,5-dihexyloxy-1,4-phenylenevinylene)] Derivatives: Synthesis and Optical Properties".
6. ACS Symposium Series 916: New Polymeric Materials, L.S. Korugic-Karasz, W.J. MacKnight and E. Martuscelli, Editors, pp. 76-89 (2005) "Impact of Cyano-Functional Group on Luminescence of Poly(*m*-phenylenevinylene) Derivatives: Its Dependence on Conjugation Length".
7. Synthetic Metals, 156, 110-116 (2006) (L. Ding, W-Y Wong, H. Xiang, S-Y. Poon and F.E. Karasz) "Photoluminescence and Electroluminescence of Oligoacetylenic Silanes and Germanes".
8. Synthetic Metals, 156, 282-286 (2006) (A. Cirpan, H.P. Rathnayake, G. Gunbas, P.M. Lahti and F.E. Karasz) "New Conjugated Materials Containing Cyano Substituents for Light-emitting Diodes".
9. J. Polym. Sci., 43, 2800-2809 (2005) (L. Liao, L. Ding, Y. Pang and F.E. Karasz) "Blue-Emitting Poly(1,3-phenylenevinylene) Derivatives: Effect of Substitution Patterns on Optical Properties".
10. J. Appl. Polym. Sci., 102, 2509-2511 (2006) (with A. Cirpan and Z.A. Aroguz) "Efficient Light Emitting Diodes from Ternary Blends of PPV-Based Copolymers".
11. Macromol. Chem. Phys., 207, 870-878 (2006) (with L. Ding, Z. Bo, Q. Chu, J. Li, L. Dai, Y. Pang and M.F. Durstock) "Photophysical and Electroluminescent Properties of Hyperbranched Polyfluorenes".

12. Adv. Funct. Mater., 17, 115-122 (2007) (with H.P. Rathnayake, A. Cirpan, Z. Delen and P.M. Lahti) "Optimizing OLED Efficacy of 2,7-Diconjugated 9,9-Dialkylfluorenes by Variation of Periphery Substitution and Conjugation Length".
13. Polym. Int., 56, 252-257 (2007) (with V.A.F. Deichmann, A. Cirpan and L. Akcelrud) "Photo- and Electroluminescent Properties of a π -Conjugated Copolymer Containing 2,2'-Bipyridyl Units".

In addition, several investigations have been completed and have been submitted for publication and are in press. These include:

14. Synthetic Metals: "Green Light-Emitting Cyano-Containing Poly[*m*-phenyleneethynylene)-*alt*-(*p*-phenyleneethynylene)]s: Synthesis and Characterization" (Li/Pang/Ding/Karasz).
15. Adv. Funct. Mater.: "Luminescence of Fluorenes 2,7-Conjugatively Extended with 1'-Pyrenylvinylene-4"-Phenylenevinylene" (Cirpan/Rathnayake/Lahti/Karasz)
16. Chem. Mater.: "Single-Molecule and Bulk Luminescence Studies of the Green Emission Band in 2,7-Bis(phenylvinylene)fluorine Derivatives" (Rathnayake/Odoi/Hammer/Barnes/Cirpan/Lahti/Karasz)
17. J. Polym. Sci.: "Synthesis and Optical Properties of Light-Emitting π -Conjugated Polymers Containing Biphenyl and Dithienosilole" (Liao/Cirpan/Pang/Karasz)

Representative of the research undertaken is a study of the photo- and electroluminescence of Eu^{3+} ions in a matrix of polyvinyl carbazole is described below.

[This work has been submitted for near term publication.]

INTRODUCTION

In complexes of Eu^{3+} ions triplet and singlet states of the relevant organic ligands transfer energy to Eu^{3+} , providing emission from the triplet state with a 100% theoretical yield. These electronic transitions of lanthanides result from different electronic distributions of 4f orbitals that are effectively shielded from external influence by the overlap of $5s^2$ and $5p^6$ orbitals.

The interaction of Eu^{3+} ions with low molecular weight organic molecules and derived complexes have been well studied, but the behavior of the ion in relation to polymer chains is less explored in terms to their solution and solid state properties. We have now studied the photophysical and electroluminescent behavior of molecular complexes of Eu^{3+} in solution and in the film form in blends with poly(vinylcarbazole) (PVK).

EXPERIMENTAL

The complexes and the polymer were characterized by FTIR spectrometry on KBr disks in the spectral range of $400\text{-}4000\text{cm}^{-1}$, with a resolution of 2cm^{-1} . Absorption spectra were obtained in THF solution and in film form. Fluorescence spectra were obtained in THF solution and in

films cast from THF onto quartz plates.

For electroluminescent studies a hole injection layer of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) was spin-coated onto an ITO layer, dried at 100°C for 1 hour under vacuum, and the filtered polymer solution was spin coated onto the PEDOT:PSS layer (nitrogen). A calcium layer (400 nm) was evaporated onto the polymer, followed by a protective coating of aluminum. The devices were characterized using a system described in the publications referred to above.

Luminescence spectra and luminescence decays were recorded with a Thermo Laser Science pulsed nitrogen laser ($\lambda_{em}=337.1$ nm; < 4 ns, FWHM) for the photo-excitation of the sample; a $\frac{1}{4}$ m emission monochromator for the spectral resolution of the luminescence emission, coupled to a diffraction grating (0.15 nm max. resolution at 546.1 nm, 1200 lines/mm, blaze at 350 nm), and glass filter to block the excitation light at the micrometer-driven entrance slit, and a fast rise time side-on photomultiplier tube at the micrometer-driven exit slit, for acquisition of the organic emission or europium emission. The entrance and exit slitwidth were set to reach a 0.4 nm spectral resolution. A Digital Oscilloscope

terminated to 255Ω or 10kΩ was used to detect the organic emission or europium emission, respectively, with 500 points for each decay curve. With these settings, the measured RC time constants of the instrumentation, for acquisition of the organic emission or europium emission, were 15ns and 642.0ns, respectively.

The tris(thenoyltrifluoroacetate)(2,2'-bipyridyl)europium(III) complex [Eu(TTA)₃Bip] was synthesized by standard techniques and the blends were prepared from the [Eu(TTA)₃Bip] complex and PVK by mixing the appropriate solutions in THF in the following ratios: 1, 2, 4 and 8%.

To obtain red emission, efficient energy transfer from the PVK to the europium salt is needed; this condition is fulfilled, due to the good overlap between PVK emission and [Eu(TTA)₃Bip] complex absorption.

FTIR absorptions of the europium salt bands at 1600cm⁻¹, (ν C-S) were observed with increase in absorption with increasing amounts of the complex in the blends.

The photophysical study was performed in the UV-Vis region using THF solutions (0.1mg/mLTHF, w/mL). It was shown that no changes in the electronic ground state or aggregate formation occur. On the other hand, the fluorescence emission spectra with excitation at 344 nm revealed

progressive changes. For pure PVK the emission is centered at 375 nm, and for pure [Eu(TTA)₃Bip] at 613 nm in solution. In all the blends incomplete energy transfer was observed since both emission peaks were present in the spectra relative to all the component ratios used.

The absorption profiles of cast films did not show any change of the absorption peak at 344nm. The emission spectra, on the other hand, had some new features. The polymeric matrix showed a red shift to 405 nm, attributed to excimer formation. Matrix emission was not seen in concentrations of Eu³⁺ higher than 2%, indicating as expected a more efficient energy transfer in the solid state as compared to the solution. We suggest that the solvent acts as an alternative non-radiative channel for triplet state decay, involving a spin-orbit coupling with solvent molecules lowering the efficiency of the solution transfer process.

The turn on voltage, the electroluminescent peak and the LED device efficiency for each blend composition were measured for all the complexes as were the corresponding EL spectra. The main findings are that there is a small red shift for the most concentrated blends, and there is complete absence of PVK emission. These observations can be attributed to the different excitation mechanisms. In EL the ion can be directly excited,

whereas in PL the emission depends of energy transfer from the ligand. The transfer from PVK is complete in EL emission; the most relevant feature of these devices. Devices built with the complex alone were unstable and it was not possible to obtain information about their behavior with the LED configuration used. However the complexes formed useful LED devices with turn on voltages in the 7 – 9 V range while the highest emission intensity was observed for the 8% w/w Eu^{3+} sample, with the film photoluminescence peaking at 617 nm, with a brightness of 66cd/m^2 at a current density of 250mA/cm^2 .

The excited state lifetimes of the PVK-Eu blends were investigated to examine the polymeric matrix effect on the optical properties of the ion. The fluorescence emission spectra of the blends in the region 570 – 640 nm were measured, together with the corresponding decay curves; that for the pure Eu^{3+} complex was also obtained.

The time resolved emission spectra of the $\text{Eu}(\text{TTA})_3\text{Bip}$ complex showed the highest intensity in the range 608 – 630 nm, which corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric dipole transition, indicating that the Eu^{3+} ion is located on non-center symmetrical sites, either in the pure state or in blended form. The profile and location of these bands in the blends

are similar to those of the pure complex, providing evidence that the “average” microsymmetry around the Eu^{3+} ion is preserved when the complex is dispersed in the polymer matrix. The lifetimes extracted from the decay curves showed that τ increases with the Eu^{3+} content in the blend, which is attributed to an energy migration process among the Eu^{3+} complexes.